

Zirconocene complexes of the sterically demanding pentaphenylcyclopentadienyl ligand, Cp^{PRO} . Synthesis and characterization of $\text{Cp}^{\text{PRO}}\text{ZrCl}_3$ and $\text{CpCp}^{\text{PRO}}\text{ZrCl}_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{Cp}^{\text{PRO}} = \eta^5\text{-C}_5(\text{C}_6\text{H}_5)_5$)

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Abstract

The synthesis, characterization and X-ray structures of two zirconium complexes of the bulky pentaphenylcyclopentadienyl ligand, Cp^{PRO} , are reported. The monocyclopentadienyl 12 electron complex, $\text{Cp}^{\text{PRO}}\text{ZrCl}_3$ (**I**), has an unusual monomeric structure in the solid state and has short Zr–ligand distances. The Lewis acidity of this complex is manifested in its ability to catalyze the [4 + 2] cycloadditions of methyl- and ethylmethacrylate to cyclopentadiene. The sandwich complex, $\text{Cp}^{\text{PRO}}\text{CpZrCl}_2$ (**II**), has more typical Zr–ligand distances, but has a more parallel arrangement of the two cyclopentadienyl rings. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The development of catalysts for promoting stereoselective organic transformations is an important goal [1]. One method that has enjoyed considerable success is the development of C_2 symmetric catalysts for the desired transformations [2–11]. Our work is directed towards developing chiral zirconocenes to promote C–C bond formation reactions like [4 + 2] cycloaddition. In our candidate complexes, asymmetry is introduced by ‘functionalizing’ one of the cyclopentadienide rings to give prochiral $\text{CpCp}'\text{ZrCl}_2$. Asymmetric complexes of the type $\text{CpCp}'\text{ZrR}(\text{OR}^*)$ can be obtained by alkylation of $\text{CpCp}'\text{ZrCl}_2$, followed by reaction with a chiral alcohol to give the alkyl–alkoxide complex. In this paper, the synthesis and characterization and solid state structures of two precursors, complexes of the pentaphenylcyclopentadienide ligand with zirconium(IV), $\text{Cp}^{\text{PRO}}\text{ZrCl}_3$ and prochiral $\text{Cp}^{\text{PRO}}\text{CpZrCl}_2$, are reported. The pentaphenylcyclopentadienide group is referred to as Cp^{PRO} owing to the resemblance of this ligand to a five bladed propeller.

2. Results and discussion

Scheme 1 shows the route to $\text{Cp}^{\text{PRO}}\text{CpZrCl}_2$, via $\text{Cp}^{\text{PRO}}\text{ZrCl}_3$.

Complex **I**, $\text{C}_5(\text{C}_6\text{H}_5)_5\text{ZrCl}_3$, is obtained by refluxing a mixture of lithium pentaphenylcyclopentadienide and zirconium tetrachloride in toluene for 2 days. Removal of the solvent and extraction of the solids with refluxing xylenes gives **I** in 88.4% yield. The pale yellow solid **I** often crystallizes from the xylenes upon cooling. The ^1H NMR of **I** (C_6D_6) shows a complex multiplet centered at δ 7.05 for the phenyl protons. The ^{13}C NMR shows one resonance for the *ortho* and *meta* carbons, suggesting that there is a process that renders these atoms equivalent on the NMR time scale or that they have coincidental chemical shifts.

The structure of $\text{Cp}^{\text{PRO}}\text{ZrCl}_3$ (Scheme 1, see Tables 1 and 2) is unusual as it is a monomeric piano stool, not undergoing the oligomerization observed in the solid state in other $\text{Cp}'\text{ZrCl}_3$ complexes [12]. The phenyl rings adopt an orientation in which they are tilted with respect to the cyclopentadienide ring, forming a five-bladed propeller-like shape. The monomeric structure is likely due to the steric demands of the Cp^{PRO} ligand; changes in geometry have been observed

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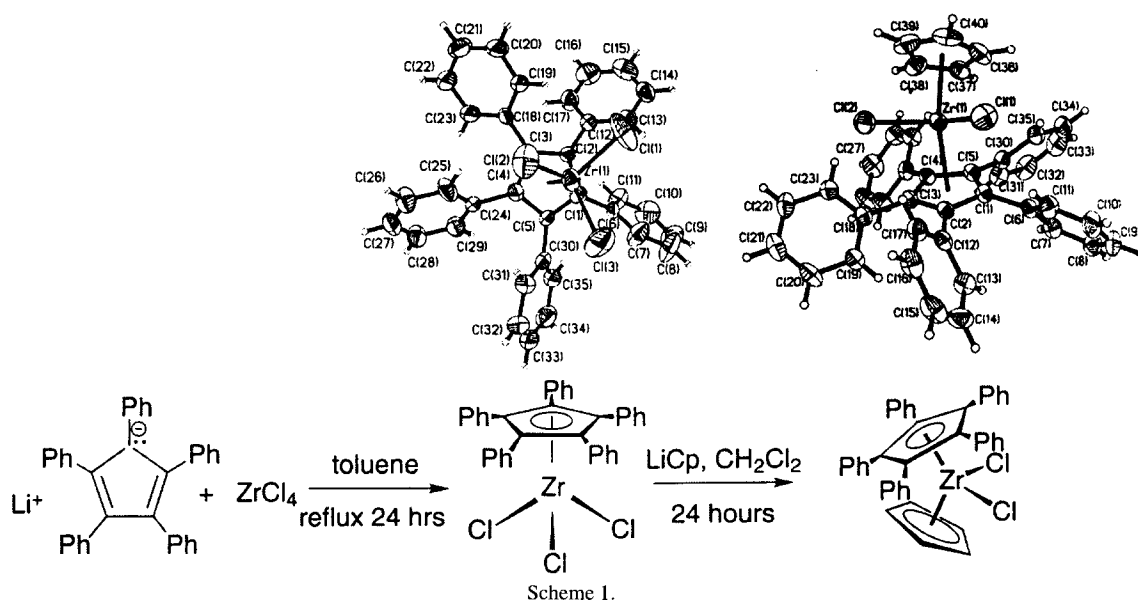


Table 1
Summary of structural parameters for **I** and **II** with comparison values

Compound	(cnt)Zr(cnt)/°	Zr–Cp(cnt)/Å	Cl–Zr–Cl/°	Zr–Cl/Å	Ref.
Cp ^{PRO} ZrCl ₃	n/a	2.222	101.2	2.34	This work
Cp ^{PRO} CpZrCl ₂	132.9	2.211 (Cp) 2.302 (Cp ^{pro})	96.9	2.42	This work
(CH ₂) ₃ (η ⁵ -C ₅ H ₄) ₂ ZrCl ₂	129.5	2.193	96.92	2.441	[20]
(η ⁵ -C ₅ H ₄ -CH ₃) ₂ ZrCl ₂	128.9			2.442	[14] and Refs. therein
Me ₂ Si(η ⁵ -C ₅ H ₄) ₂ ZrCl ₂	125.4	2.197	97.98	2.435	[14]
((SiMe ₃) ₃ C ₅ H ₂) ₂ ZrCl ₂	135.41	2.246	96.2	2.429	[15]

Table 2
X-ray collection data for **I** and **II**

Compound	I	II
Empirical formula	C ₃₅ H ₂₅ Cl ₃ Zr	C ₄₀ H ₃₀ Cl ₂ Zr
Formula weight	643.12	672.76
Crystal size (mm)	0.4 × 0.4 × 0.1	0.50 × 0.59 × 0.50
Space group	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
Cell constants		
<i>a</i> (Å)	16.680(3)	12.4266(6)
<i>b</i> (Å)	10.1308(15)	14.0366(7)
<i>c</i> (Å)	17.835(3)	17.7939(9)
<i>β</i> (°)	N/a	92.9590(10)
Cell volume (Å ³)	3013.8(8)	3099.6(3)
<i>Z</i>	4	4
Diffractionmeter used	SMART CCD area detector	SMART CCD area detector
Radiation	Mo	Mo
<i>R</i> 1 (3422 <i>F</i> > 4σ _{<i>F</i>})	0.0387	0.0579
<i>R</i> 1 (7153 all)	0.1284	0.1335
<i>wR</i> 2	0.0499	0.1130 0.1593

upon substitution of a Cp^{PRO} ligand for a Cp ligand [13]. Also, complex **I** is formally a 12 electron complex; the electron deficiency is reflected in the shorter metal–cyclopenta-

dienide and metal–chloride bonds. The Cp^{PRO} centroid and the chloride ligands in **I** are about 8 pm closer to the Zr atom than in the 16 electron complex **II**.

Metathesis of **I** with LiCp in dichloromethane for 24 h gives a pale yellow suspension. Removal of the solvent and extraction of the residue with dichloromethane gives the pale yellow–green product CpCp^{PRO}ZrCl₂ (**II**) in 95.1% yield. Analytically pure yellow–green crystalline material is obtained by Soxhlet extraction of the crude with refluxing xylenes resulting in a final yield of 77%. Complex **II** is sparingly soluble in toluene and benzene and more soluble in polar organic solvents such as chloroform and dichloromethane. In the ¹H NMR (CD₂Cl₂), a singlet is observed for the C₅H₅ at δ 6.60, and the phenyl ring protons are observed as multiplets centered at δ 6.98 and δ 7.09 ppm. The ¹³C{¹H} NMR is also consistent with the given formulation.

The X-ray crystal structure of **II** (Tables 1 and 2) shows a systematic variation of the Zr–C distances; the average Zr–C distance to the pentaphenylcyclopentadienyl ligand (260.4 pm) is longer than that to the cyclopentadienyl group (251.2 pm). The Zr–Cp(cnt) distance (221.1 pm) is about 9 pm shorter than the Zr–Cp^{PRO}(cnt) distance (230.2 pm). In addition, the distances to each ring show significant variation, with those Zr–C distances above the ‘pocket’ being longer

than those away from the 'pocket' by about 5 pm. The centroid–Zr–centroid angle of 132.9° is larger than that of $(\text{Me-Cp})_2\text{ZrCl}_2$ (128.9°) [14] but not as open as the 135.4° in hexakis(trimethylsilyl)zirconocene dichloride [15]. The distances to the chloride ligands (242 pm) are somewhat smaller than those for zirconocene dichloride (244.3 pm [14]) as is the C11–Zr–Cl2 angle of (96.69°) when compared to that of other zirconocene dichlorides (98°). The structural similarities between the Cp^{PRO} complex and the severely hindered hexakis(trimethylsilyl)zirconocenedichloride [15] complexes reflect like steric effects; however, the lack of a second bulky ligand in **II** should result in greater reactivity by allowing attack from the side of the unsubstituted Cp ligand.

As a 12-electron complex, **I** is expected to show Lewis acidity as observed in other such low-electron count complexes [11,16–19]. Room temperature chloroform- D_2 , dichloromethane and benzene- D_6 solutions of cyclopentadiene and a dienophile (methyl- or ethylmethacrylate) containing 3–4 mol% of **I** all undergo a slight color change within an hour of preparation compared to solutions of **I** alone. Cyclization is observed in these solvents, with *endo–exo* selectivity similar to that observed by previous workers [6]. Polymerization of methyl methacrylate is also observed under these conditions. We are currently investigating the activity of **I** with other dienophiles and dienes to ascertain the scope, selectivity and efficacy of these and related complexes in catalyzing the [4 + 2] cycloaddition reaction.

Preliminary work in our laboratories indicates that complex **II** undergoes alkylation with Grignard reagents, unlike the hexakis(trimethylsilyl)zirconocenedichloride [15] complex. Further studies are in progress to explore the substitution chemistry of this complex with the goal of preparing zirconocenes of C_1 symmetry.

3. Experimental

3.1. General considerations

Most of the compounds described were air sensitive and were prepared with use of either Schlenk or high-vacuum techniques. Solid compounds were manipulated in a Vacuum Atmospheres Corp. (VAC) HE-43 Dri-Lab with an HE-63P Pedatrol pressure regulator and HE-393 Dri Train. The inert gas used in the glovebox and Schlenk and vacuum lines was either nitrogen or argon, which was further purified by passage through activated Chemalog R3-11 catalyst and activated 4 Å molecular sieves. Solvents were all reagent grade or better and were further purified by standard techniques [21]. Pentaphenylcyclopentadiene and the lithium salt were prepared as previously described [22] with minor modifications.

3.2. Physical measurements

^1H and ^{13}C NMR spectra were obtained with Bruker AM-400 or AM-300 spectrometers. Proton NMR spectra were referenced by either the residual proton resonance or internal tetramethylsilane. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

3.3. $\text{C}_5(\text{C}_6\text{H}_5)_5\text{ZrCl}_3$ (**I**)

Pentaphenylcyclopentadienyltrichlorozirconium (**I**) was prepared by refluxing 3.462 g of lithium pentaphenylcyclopentadienide with 2.651 g of zirconium tetrachloride for ~24 h in 50 ml dry xylene. The solvent was removed in vacuo and the reddish brown solid was then extracted with 50 ml of dry xylene for 24 h in a Soxhlet type extractor. The solvent was removed in vacuo to give a yellow solid and the remaining residue extracted for an additional 24 h. The total product obtained from two successive extractions was 4.35 g with an 88.4% yield. Analytically pure crystalline material may be obtained by slow cooling of the xylenes solution. ^1H NMR (CDCl_3): overlapping multiplets centered at δ 7.2. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz): $\text{C}_5(\text{C}_6\text{H}_5)$, δ 128.0; $\text{C}_5(\text{C}_6\text{H}_5)$, *ipso-C*, δ 133.8; *o-C* δ 131.7; *m-C*, δ 132.0; *p-C*, δ 127.8. Analytical data %found(%calc.): C, 65.25(65.36); H, 4.10(3.92).

3.3.1. X-ray structure of **I**

The sample crystallized as yellow hexagonal plates from a slowly cooled, hot xylenes solution. One plate of approximately 0.4 mm by 0.4 mm by 0.1 mm was sampled by X-ray diffraction with graphite monochromated $\text{Mo K}\alpha$ radiation up to $\theta = 28.28^\circ$ by a Bruker SMART CCD area detector mounted on a three-circle goniostat. The diffraction pattern of the crystal was consistent with a $\text{Pna}2_1$ orthorhombic space group with cell dimensions of $a = 16.680(3)$, $b = 10.1308(15)$, and $c = 17.835(3)$ Å. 31756 observations were measured and averaged with their symmetry-related reflections to form 7153 unique reflections. Of the unique reflections, 3422 reflections had an intensity $I > 2\sigma_I$, $R_{\text{int}} = 0.0982$. The structure was solved by Patterson methods and subsequently refined to convergence with the SHELXTL software package. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were isotropically refined from initial ideal positions. The final agreement statistic of 3422 structure factor amplitudes having $F > 4\sigma_F$ were $R1 = 3.87\%$ based on F , and $wR2 = 4.99\%$ based on I .

3.4. $\text{CpCp}^{\text{PRO}}\text{ZrCl}_2$ (**II**)

Cyclopentadienyl(pentaphenylcyclopentadienyl)dichlorozirconium (**II**) was prepared by stirring 4.120 g of pentaphenylcyclopentadienyltrichlorozirconium and 0.451 g of lithium cyclopentadienide in 30 ml of dry dichloromethane for 24 h at room temperature. Removal of the solvent in vacuo gave a yellow brown solid. The solid was then Soxhlet

extracted with 60 ml of dry dichloromethane to yield 4.021 g of **II** as a pale yellow powder in a 95.1% yield. Analytically pure crystalline material may be obtained by slow cooling of a hot xylenes solution of **II**. ^1H NMR (CDCl_3): C_5H_5 , $\delta = 6.55$ (s); $\text{C}_5(\text{C}_6\text{H}_5)_5$, $\delta 7.10$ (m), $\delta 6.94$. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): C_5H_5 , $\delta 118.6$; $\text{C}_5(\text{C}_6\text{H}_5)_5$, *ipso* C $\delta 133.5$; *m*-C $\delta 132.0$; *p*-C $\delta 127.5$; *o*-C $\delta 127.3$; $\text{C}_5(\text{C}_6\text{H}_5)_5$, $\delta 129.9$. Analytical data, %found(%calc.): C, 71.40(71.41); H, 4.49(4.49).

3.4.1. X-ray structure of **II**

The sample crystallized as dark green–violet prisms from a slowly cooled hot xylenes solution. One prism of approximately 0.5 mm by 0.5 mm by 0.5 mm was sampled by X-ray diffraction with graphite monochromated Mo $K\alpha$ radiation up to $\theta = 28.28^\circ$ by a Bruker SMART CCD area detector mounted on a three-circle goniostat. The diffraction pattern of the crystal was consistent with a $P2_1/c$ monoclinic space group with cell dimensions of $a = 12.4266(6)$, $b = 14.0366(7)$, and $c = 17.7939(9)$ Å, and $\beta = 92.9590(10)^\circ$. 30932 observations were measured and averaged with their symmetry-related reflections to form 7076 unique reflections. Of the unique reflections, 4562 reflections had an intensity $I > 4\sigma_I$. $R_{\text{int}} = 0.1192$ before correction factors were refined for absorption and decay, and $R_{\text{int}} = 0.0456$ after correction. The structure was solved by Patterson methods and subsequently refined to convergence with the SHELXTL software package. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were isotropically refined from initial ideal positions. The final agreement statistics of 4562 structure factor amplitudes having $F > 4\sigma_F$ were $R1 = 5.79\%$ based on F , and $wR2 = 13.35\%$ based on I .

3.5. Cycloaddition studies

NMR studies were performed by preparing a solution containing the solvent, the diene (ca. 0.8 M) and dienophile (0.3 M). This solution is split in the glove box and placed into two NMR tubes fitted with rotationally symmetric valves. One of these tubes is loaded with the catalyst candidate (typ-

ically 4 mol%) and the other used as a control. NMR spectra were obtained periodically and analyzed using peak areas and spectra of the known products.

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